

Claims:

1. Process for obtaining bulk gallium-containing nitride monocrystals from supercritical ammonia-containing solution in the presence of a mineralizer, characterized in that in a pressurized reaction vessel - using ammonia as solvent and Group I element azides and optionally Group II element azides as mineralizer, a supercritical ammonia-containing solution including Group I and optionally Group II element ions is first obtained to dissolve next a gallium-containing feedstock at dissolution temperature and/or dissolution pressure and then the desired gallium-containing nitride is crystallized from the supercritical solution on the surface of at least one seed at the crystallization temperature and/or crystallization pressure, wherein the crystallization temperature and/or crystallization pressure is selected according to the temperature coefficient of solubility and pressure coefficient of solubility of the desired gallium-containing nitride to be crystallized.
2. Process for obtaining bulk gallium-containing nitride monocrystals from supercritical ammonia-containing solution in the presence of Group I and optionally Group II element-containing mineralizer, characterized in that when gallium-containing nitride has a negative temperature coefficient of solubility and a positive pressure coefficient of solubility in supercritical ammonia-containing solution, in the presence of Group I and optionally Group II element-containing mineralizer, in a pressurized reaction vessel - using Group I element azides and optionally Group II element azides as mineralizers - supercritical ammonia-containing solution including Group I and optionally Group II element ions is first obtained to dissolve next a gallium-containing feedstock at dissolution temperature and/or dissolution pressure and then gallium-containing nitride is crystallized from the supercritical solution on the surface of at least one seed by means of bringing the temperature to crystallization temperature and/or the pressure to crystallization pressure, the crystallization temperature being higher than the dissolution temperature and/or the crystallization pressure being lower than the dissolution pressure at least at the crystallization zone of the pressurized reaction vessel, where

the seed is placed – so that super-saturation of the supercritical solution with respect to the seed is achieved - and then the super-saturation of the supercritical solution is maintained at the level at which spontaneous crystallization of the nitride may be neglected, while crystallization of the desired gallium-containing nitride is carried out on the seed.

3. Process according to claim 1 or 2, characterized in that the gaseous nitrogen, produced during the decomposition of the azide, is at least partially evacuated from the system before the re-crystallization step is started.
4. Process according to any one of the preceding claims 1 to 3, characterized in that as a gallium-containing nitride - the nitride having a general formula $Al_xGa_{1-x}N$, where $0 \leq x < 1$ is crystallized.
5. Process according to any one of the preceding claims 1 to 4, characterized in that the azide mineralizers are selected from the group consisting of LiN_3 , NaN_3 , KN_3 , CsN_3 and mixtures thereof.
6. Process according to any one of the preceding claims 5, characterized in that the mineralizer used contains at least one compound selected from the group consisting of LiN_3 , NaN_3 , KN_3 and CsN_3 .
7. Process according to the claim 6, characterized in that the mineralizer contains NaN_3 and KN_3 mixed in arbitrary molar ratio.
8. Process according to the claim 6, characterized in that the mineralizer contains NaN_3 and LiN_3 mixed in arbitrary molar ratio.
9. Process according to the claim 6, characterized in that the mineralizer contains KN_3 and LiN_3 mixed in arbitrary molar ratio.
10. Process according to the claim 6, characterized in that the mineralizer contains also Group I and optionally Group II element-containing compound(s) other than azides.

11. Process according to any one of the preceding claims 1 to 10, characterized in that Group I element azides are introduced into the system in a molar ratio of azides to ammonia ranging from 1:200 to 1:2.
12. Process according to any one of the preceding claims 1 to 11, characterized in that a seed crystal with at least a crystalline layer of Group XIII element nitride, preferably gallium-containing nitride, having a dislocation density less than $10^7 / \text{cm}^2$ is used.
13. Process according to any one of the preceding claims 1 to 12, characterized in that a structure having a number of surfaces spaced adequately far from each other, arranged on a primary substrate and susceptible to the lateral overgrowth of crystalline nitrides is used as a seed.
14. Process according to any one of the preceding claims 1 to 13, characterized in that a monocrystalline nitride layer is obtained having the same or better quality as it gets thicker.
15. Process according to claims 13 or 14, characterized in that the seed contains the primary substrate made of a crystalline nitride of Group XIII elements.
16. Process according to claim 15, characterized in that the seed contains the primary substrate made of gallium nitride – GaN.
17. Process according to claim 15, characterized in that the seed contains the primary substrate made of a crystalline material such as sapphire, spinel, ZnO, SiC or Si, wherein the primary substrate made of the material reacting with a supercritical ammonia-containing solution is covered with a protective layer, preferably made of a nitride containing Group XIII elements or metallic Ag, prior to formation of a monocrystalline nitride layer.
18. Process according to any one of the preceding claims 1 to 3, characterized in that the bulk nitride monocrystals obtained consist essentially of gallium nitride – GaN.

19. Process according to any one of the preceding claims 1 to 3, characterized in that the bulk nitride monocrystals obtained contain any of the following elements: Ni, Cr, Co, Ti, Fe, Al, Ag, Mo, W, Si and Mn.
20. Process according to any one of the preceding claims 1 to 3, characterized in that some surfaces of the seed are covered with a mask layer prior to formation of a monocrystalline nitride layer.
21. A bulk nitride monocrystal obtained by a process according to any one of the preceding claims 1 to 20.
22. Use of the bulk nitride monocrystal according to claim 21 as substrate for epitaxy.
23. Use according to claim 22, characterized in that the bulk nitride monocrystal has at least one epitaxial layer of the same or different Group XIII element nitride, deposited by MOCVD or HVPE or else MBE method - as a template for opto-electronic devices.
24. Use according to claim 23, characterized in that MOCVD or HVPE or else MBE nitride layers are doped with various dopants.
25. Mineralizer used for supercritical ammonia-containing solution which comprises at least one compound selected from the group consisting of LiN_3 , NaN_3 , KN_3 , and CsN_3 .
26. Mineralizer according to the claim 25, which contains NaN_3 and KN_3 in arbitrary molar ratio of NaN_3 to KN_3 .
27. Mineralizer according to the claim 25, which contains NaN_3 and LiN_3 in arbitrary molar ratio of NaN_3 to LiN_3 .
28. Mineralizer according to the claim 25, which contains KN_3 and LiN_3 in arbitrary molar ratio of KN_3 to LiN_3 .
29. Mineralizer according to the claim 25, which contains NaN_3 , KN_3 and LiN_3 in arbitrary molar ratio of NaN_3 to KN_3 and LiN_3 .

30. Mineralizer according to the claim 25, which further contains Group I and optionally Group II element-containing compound(s) other than azides and/or Group I element, and/or Group II element.